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研究论文

非金属氢化物pK_a定量结构性质关系(QSPR)研究

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摘要 采用Tomasi的极化统一模型对非金属氢化物H_mA在水相条件下进行从头算, 选取与A原子电子密度相关的7个量子化学参数对氢化物pK_a进行多元回归和逐步回归, 建立的QSPR方程相关系数R分别为0.9984和0.9947, 标准偏差s分别为1.7349和2.3618, 留一法交叉验证的结果则为R=0.9689和0.9895, s=7.5985和3.3118, 表明由逐步回归建立的方程具有更高的预测可靠性, 同时也表明逐步回归分析引入的原子净电荷数NC、电荷布居数TP和最低未占分子轨道能级E_{LUMO} 3个参数是影响H_mA酸强度的关键参数. 对NC, TP和ELUMO的物理意义及其对H_mA pK_a影响的深入分析表明, 这3个参数是决定A原子电子密度大小的主要因素, E_{LUMO}和TP则分别是同主族氢化物和同周期氢化物酸性强弱递变的决定因素.

关键词 非金属氢化物 pK_a 极化统一模型 从头算 电子密度 定量结构性质关系

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Quantitative Structure Property Relationship Study on pK_a of Nonmetal Hydrides

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Abstract Tomasi's Polarized Continuum Model(PCM) and *ab initio* method were applied to calculate quantum chemical parameters for H_mA in water. Seven quantum chemical parameters, which were correlated with electronic density of the center atom A, were used to derive two equations of QSPR for the pK_a of H_mA by multiple linear regression(MLR) and stepwise regression(SR) respectively, and the correlated coefficient R and standard derivation s of the MLR and SR equations are 0.9984, 0.9947 and 1.7349, 2.3618, respectively. By the leave-one-out method prediction, the R and s of MLR and SR equation are 0.9689, 0.9895 and 7.5985, 3.3118, respectively. The results show that the SR equation, which is composed of three parameters, is the best in prediction, and the three parameters, NC(Net Charge), TP(Total Population) and E_{LUMO} are the key factors affecting the acid intensity of H_mA. The physical meaning and the influence of the three parameters on pK_a of H_mA were investigated. The study indicates that NC, TP and E_{LUMO} are the main factors which affect the electronic density of center atom A; E_{LUMO} and TP are the decisive factors affecting the change of acid intensity of H_mA in the same group and period respectively.

Key words Nonmetal hydride; pK_a; Polarized continuum model; *Ab initio*; Electron density; Quantitative structure property relationship(QSPR)

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